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High quality single phase samples of $Ba_{1-x}K_xBiO_3$ (BKBO) have been made across the range of compositions from $0 < x < 0.5$. Powder x-ray diffraction data indicates pure single phase materials for all potassium concentrations. Samples with $x < 0.35$ are nonsuperconducting while those with $x > 0.35$ show sharp superconducting transitions from both resistivity and magnetization measurements. Care during sample preparation is vital for obtaining quality samples of this material.

The compound $Ba_{1-x}K_xBiO_3$ (BKBO), discovered in 1988,[1,2] is unique among the high T_c oxide superconductors. Since it has no copper, the copper-oxygen planes which play important roles in other compounds are missing here. Furthermore, this material has a true cubic perovskite structure so there is no anisotropy. Because of these two differences, this compound provides additional insights into the mechanisms of high T_c superconductivity.

Samples of BKBO for $0 < x < 0.5$ were prepared from stoichiometric mixtures of BaO, KO_2 and Bi_2O_3 using a multi-stage N_2 and O_2 annealing process.[3] In order to obtain single phase samples with good superconducting properties with this method there are several hurdles which must be overcome.

The first major problem is the reactivity of the BaO and KO_2 with moisture, which decompose quickly into various hydroxides. Since commercially available BaO often contains significant amounts of these hydroxides, fresh BaO was calcined at 1000°C for 24 h under active vacuum from $BaCO_3$ as needed. The BaO and KO_2, both in lump form, were exposed to air briefly only when removed from the oven or when being weighed. The three oxides were then placed into a glove bag filled with high purity N_2, ground, and packed into a pellet die before being removed from the glove bag. After pressing, these pellets were immediately placed into a tube furnace under a controlled flow of the N_2. With these precautions very little moisture was introduced to the starting material.

The second major problem was obtaining single phase samples with sharp superconducting transitions. To this end, the samples were cycled through a two stage annealing process. In the first stage of this cycle, the pellets were ramped to 700°C in 3 h in flowing N_2 in a quartz tube, held for 1 h and then quenched to room temperature to avoid phase separation problems common to BKBO. The gas flow was then switched to dried O_2 and the samples ramped to 450°C in 2 h, held for 2 h and then slowly cooled back to room temperature. The samples were reground and this standard cycle repeated twice to promote sample homogeneity.

The samples at this point were a uniform deep blue for $x > 0.3$ and a dull brown for $x < 0.2$ but unfortunately they had poor mechanical properties and broad superconducting transitions. To remedy this, the samples were run through one final cycle with the N_2 annealing temperatures elevated to slightly below the melting point.

X-ray powder diffraction patterns show single phase material for all values of x. For $x > 0.3$ there are slight shoulders on the peaks, showing minor phase separation despite the rapid cool. These samples all have a deep blue color, although only the samples with $x > 0.35$ turn out to be superconducting. For $x < 0.3$ there is significant line broadening, indicative of the monoclinic distortion seen in this material.[3] These samples are brown in color.

Magnetization measurements as a function of temperature were done using a commercial SQUID Magnetometer. Figure 1 shows $4\pi M$ vs T data for various compositions. Superconducting samples with $x \geq 0.36$ have transition widths (90%-10%) typically on the order of 3K with over 90% shielding. T_c reaches a maximum of 29 K at $x = 0.4$ and decreases as x is changed in either direction from this value. At $x \leq 0.34$ the behavior is markedly different. There is still a diamagnetic signal with a $T_c \sim 27$ K but the

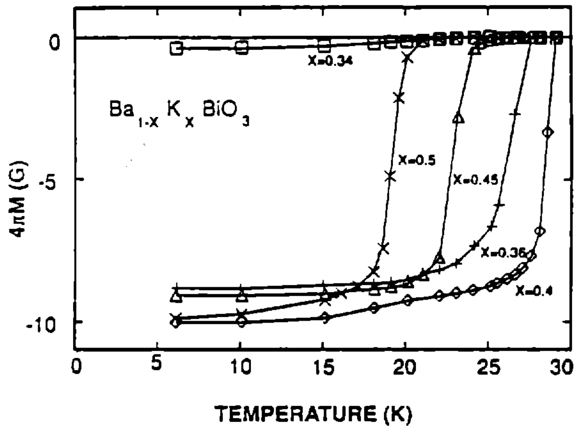

Figure 1. Zero field cooled DC magnetization measurements for H = 10 Oe.

shielding fraction drops to 4% at $x = 0.34$ and further to 0.5% at $x = 0.30$. Thus there is still some variation across the sample but the vast majority is within a percent or two of the nominal composition.

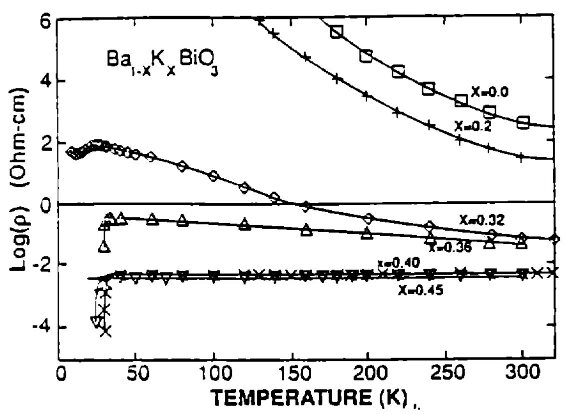

Figure 2. The log(resistivity) vs temperature. Potassium concentrations are indicated on the graph.

More interesting than the magnetization is the normal state resistivity. Data was taken using a standard 4-probe AC resistivity technique with a current of 0.1 mV at 23 Hz. Leads were attached using silver epoxy with contact resistances of less than an Ohm. Figure 2 shows a tremendous variation in log(ρ) vs T for various compositions. The samples with $x = 0.0$, 0.1, and 0.2 show a semiconducting $\exp(E_g/k_BT)$ behavior with the energy gap given by $E_g = 0.2$ eV. In general, as x increases, ρ decreases. In addition,

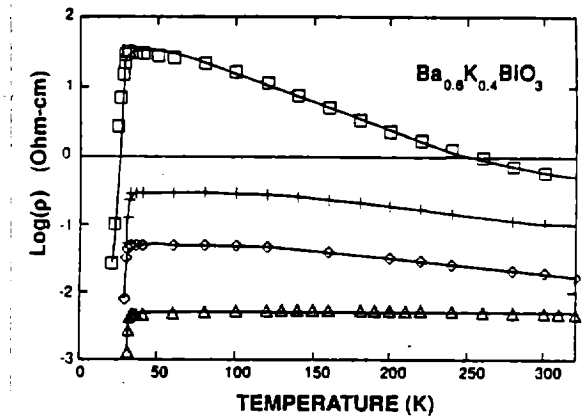

Figure 3. Log(resistivity) vs temperature for four samples with $x = 0.4$.

the temperature dependence of ρ is sensitive to processing, as shown in Figure 3 for four samples with $x = 0.4$. The sample with $x = 0.4$ with the highest resistivity, along with the samples at $x = 0.32$ and $x = 0.36$ can be fit with $\exp(T_o/T)^{1/4}$, indicative of variable range hopping which has been seen previously in this material.[4] The sample with $x = 0.4$ with the lowest resistivity does not show this behavior but rather reaches a maximum near 170 K and then decreases.

These results indicate that the dominant mechanism for transport depends not only on the Ba:K ratio but also on the details of the microstructure. Variable range hopping is seen in some of the superconducting samples, but this behavior is not intrinsic to BKBO.

Acknowledgments

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